

# Phase separation and electron pairing in repulsive Hubbard clusters

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Exact thermal studies of small (4-site, 5-site and 8-site) Hubbard clusters with local electron repulsion yield intriguing insight into phase separation, charge-spin separation, pseudogaps, condensation, in particular, pairing fluctuations away from half filling (near optimal doping). These exact calculations, carried out in canonical (i.e. for fixed electron number  $N$ ) and grand canonical (i.e. fixed chemical potential  $\mu$ ) ensembles, monitoring variations in temperature  $T$  and magnetic field  $h$ , show rich phase diagrams in a  $T$ - $\mu$  space consisting of pairing fluctuations and signatures of condensation. These electron pairing instabilities are seen when the onsite Coulomb interaction  $U$  is smaller than a critical value  $U_c(T)$  and they point to a possible electron pairing mechanism. The specific heat, magnetization, charge pairing and spin pairing provide strong support for the existence of competing (paired and unpaired) phases near optimal doping in these clusters as observed in recent experiments in doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$  high  $T_c$  superconductors.

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Since the discovery of the high temperature superconductors (HTSCs), there has been an intense debate about a possible electron (or hole) pairing mechanism. Early on, P. W. Anderson [1] suggested that the large positive onsite Coulomb interaction in the Hubbard model should contain the key to some of the perplexing physics observed in the HTSCs. Although it is next to impossible to list every single effort related to testing the above assertion, important progress has been made in attempts to obtain a better understanding of the physical properties of these materials [2, 3, 4, 5, 6, 7]. The bad metallic behavior and small correlation length of dynamical spin fluctuations (different from conventional superconductors) make HTSCs [8] a suitable platform to examine the role of local interactions. Exact studies of the Hubbard clusters placed in magnetic field  $h$  are fundamental for understanding the nature of magnetism and corresponding spin gaps in various cluster geometries [9, 10]. Repulsive interactions can lead to phase separation, electron pairing and ground state superconductivity in certain mesoscopic structures [11, 12]. In our opinion, thermal properties of small clusters with strong correlations have not been fully explored, although there have been numerous exact calculations [13, 14], and the present study is an attempt to fill this void.

Our recent work [15] indicates that Hubbard clusters, when connected to a particle reservoir and a thermal bath, possess a vivid variety of interesting thermal and physical properties, that could pave the way for a new class of tunable materials. These inferences were drawn by not only carrying out exact diagonalizations of the many-body Hamiltonian, but also using these eigenvalues in a statistical ensemble to study thermal and other transitions, by monitoring, for example, susceptibilities, i.e. *fluctuations*. The many-body nature of these correlated problems is at least partly hidden in statistical fluctuations and it is no wonder that these fluctuations

give rise to intriguing results. The crossovers and transitions between various phases, that we identify at finite and zero temperatures, are found by monitoring the corresponding thermal and ground state properties without taking the thermodynamic limit. The results described in this paper provide new insights into the physics of the 4-site as well as larger (repulsive) Hubbard clusters.

These attempts may be questioned since they appear not to comply with the standard applications of statistical mechanics with respect to the thermodynamic limit. However, for finite systems, it is necessary to re-evaluate these ideas and a paradigm shift in our thinking may be necessary. We have already shown that in such finite systems, one can define and identify various transitions and phase boundaries by monitoring maxima and minima in susceptibilities [15]. As synthesis techniques improve at a rapid rate, it has become possible to synthesize isolated clusters and hence it is clear that we need not always look at the thermodynamic limit. Finite, mesoscopic structures (i.e. clusters containing a few atoms) in suitable topological forms will be realistic enough to synthesize and extract fascinating physical properties. Also, since the HTSCs are known to consist of (stripes and possibly other) inhomogeneities [16], it is possible that these cluster studies may be able to capture some of the essential physics of the HTSCs. The following is a list of properties, resulting from our exact (4-site, 5-site and 8-site) Hubbard cluster studies, that is shared with the HTSCs.

- Phase diagrams in a temperature-chemical potential (doping) plane and the presence of a multitude of fascinating phases, including Mott-Hubbard like paramagnetic and antiferromagnetic phases [15].
- Vanishing of a charge gap at a critical set of parameters and thereby providing an effective attraction leading to onset of electron charge pairing ( $2e$ ) at a critical temperature  $T_c^P$ .

- Spin pairing at a lower temperature ( $T_s^P$ ) and hence the formation of rigidly bound spin pairs in a narrow, critical region of doping.
- Low temperature specific heat peak, reminiscent of the experimental, low temperature specific heat behavior in the HTSCs [17].
- Temperature vs  $U$  phase diagram, indicating the pressure effect on the superconducting transition temperature as seen in recent experiments [18].
- The presence of a dormant magnetic state, lurking in the above narrow, critical region of doping, that could be stabilized by either applying a magnetic field, going above the spin pairing temperature, or changing the chemical potential, as seen in a recent, notable experiment [19].
- The opening of a pseudogap above the pairing temperature, as observed in NMR experiments, in both hole and electron doped cuprates [20].
- Larger clusters with different topologies and higher dimensionality illustrating how the above properties get scaled with size.

In what follows, we will address the similarities listed above using the many-body eigenvalues of the Hubbard clusters (*with energies measured in units of  $t$ , the hopping parameter*) in combination with statistical mechanics. The grand partition function  $Z$  (where the number of electrons  $N$  and the projection of spin  $s^z$  can fluctuate) and its derivatives are calculated exactly without taking the thermodynamic limit. The response functions related to electron or hole doping (i.e. chemical potential  $\mu$ ) or magnetic field  $h$  demonstrate clearly observable, prominent peaks paving the way for strict definitions of Mott-Hubbard (MH), antiferromagnetic (AF), spin pseudogaps and related crossover temperatures [15, 21].

Our exact studies of 4-site clusters indicate a net electron attraction leading to the formation of bound electron pairs and possible condensation at finite temperature for  $U < U_c(T)$  (i.e. suggestive of superconductivity) [15, 21]. This pairing mechanism in the 4-site cluster, at  $1/8$  hole doping ( $\langle N \rangle \approx 3$ ) away from half filling, exists when the onsite Coulomb interaction  $U$  is less than an analytically obtained critical value,  $U_c(T = 0) = 4.584$  (in units of the hopping parameter  $t$ ). This critical value, first reported in Ref. [21], is temperature dependent and can be associated with an energy gap (order parameter) which becomes negative below  $U_c(T)$  implying that it is more energetically favorable to have a bound pair of electrons (or holes) compared to two unpaired ones at an optimal chemical potential (or doping level)  $\mu = \mu_P = 0.658$ . Above this critical value  $U_c(T)$ , there is a Mott-Hubbard like gap that exists when the average particle number  $\langle N \rangle \approx 3$ ; this gap decreases monotonically as  $U$  decreases and vanishes at  $U_c(T)$ . The vanishing of the gap can be directly linked to the *onset of pair formation*. There is

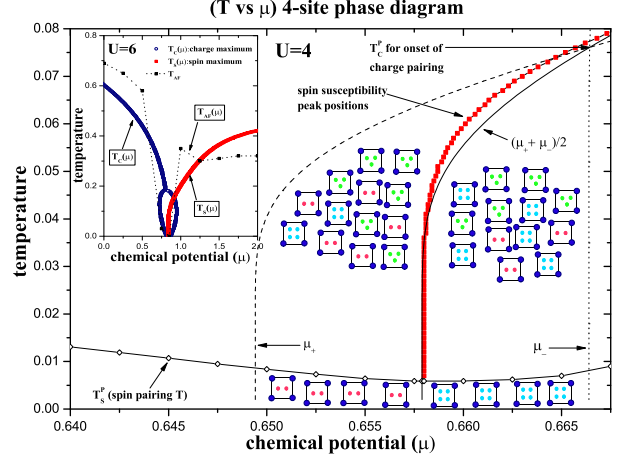


FIG. 1: The  $T$ - $\mu$  phase diagram near  $\mu_P = 0.658$  ( $\langle N \rangle \approx 3$ ) at  $U = 4$  for the 4-site cluster. The inset shows a corresponding section (at a different scale) of the  $T$ - $\mu$  phase diagram for  $U = 6$ . For  $U = 4$ , note how the paired states condense at low temperature with a nonzero pair binding energy, while at higher temperatures, unpaired states begin to appear. This picture supports the idea that there is inhomogeneous, electronic phase separation here. When  $U$  is higher than  $U_c(0) = 4.584$ , these inhomogeneities disappear and a Mott-Hubbard like stable paramagnetic insulating region results around optimal doping. Note how the (low temperature) region around optimal doping changes from a pairing phase at  $U = 4$  to a paramagnetic phase at  $U = 6$  (inset) with charge-spin separation as described in the text and Ref. [15].

an interval (width) around  $\mu_P$ , where the pairing phase competes with a phase (having a high magnetic susceptibility) that suppresses pairing at ‘moderate’ temperatures.

An enlarged view of the  $T$ - $\mu$  phase diagram, for the 4-site cluster near  $\mu_P$ , is shown in Fig. 1. This exact phase diagram (at  $U = 4$ ) in the vicinity of the optimally doped ( $N \approx 3$ ) regime has been constructed using the ideas described in the text and Ref. [15]. The electron pairing temperature,  $T_c^P$ , identifies the onset of charge pairing. As temperature is further lowered, spin pairs begin to form at  $T_s^P$ . At this temperature (with zero magnetic field), spin susceptibilities become very weak indicating the disappearance of the  $\langle N \rangle \approx 3$  states. Below this spin pairing temperature, only paired states are observed to exist having a certain rigidity, so that a nonzero magnetic field or a finite temperature is required to break the pairs. From a detailed analysis, it becomes evident that the system is on the verge of an instability; the paired phase competing with a phase that suppresses pairing which has a high, zero-field magnetic susceptibility. As the temperature is lowered, the number of  $\langle N \rangle \approx 3$  (unpaired) clusters begins to decrease while a mixture of (paired)  $\langle N \rangle \approx 2$  and  $\langle N \rangle \approx 4$  clusters appears. Interestingly, the critical doping  $\mu_P$  (which corresponds to a filling factor of  $1/8$  hole-doping away from half filling), where the

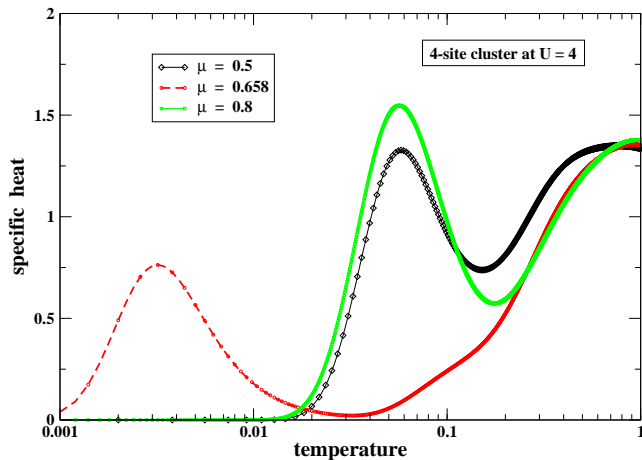


FIG. 2: Specific heat vs temperature at  $U = 4$ , calculated in the grand canonical ensemble for the 4-site cluster at several doping values near the critical doping,  $\mu_P \approx 0.658$ . Note how the low temperature peak shifts to higher temperatures when the doping is changed from its critical value.

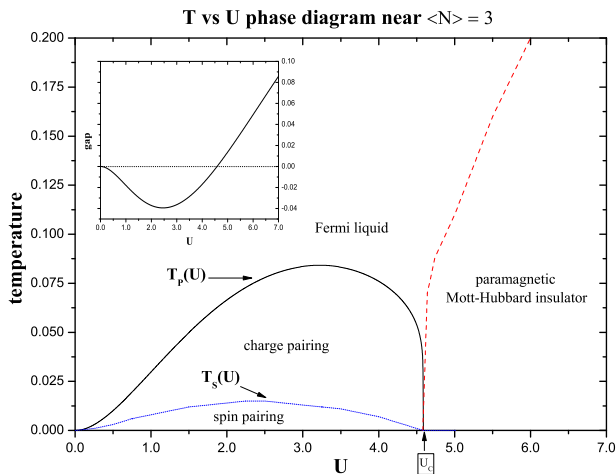


FIG. 3:  $T$  vs  $U$  phase diagram for the optimally doped 4-site clusters, based on our exact calculations. The inset shows the charge gap as a function of  $U$  at zero temperature. A negative charge gap implies charge pairing.

above pairing fluctuations take place when  $U < U_c(T)$ , is close to the doping level near which numerous intriguing properties have been observed in the hole-doped HTSCs.

Specific heat calculations (Fig. 2), associated with energy fluctuations, also provide further support for an electronic phase change at low temperature. There is strong evidence for pair condensation, from specific heat calculations shown in the figure. As seen in this figure, there is a well separated, low temperature peak at  $\mu_P = 0.658$  (around 40 K, if the hopping parameter is set to 1 eV and  $U$  to 4 eV). This peak, which shifts to higher temperatures when the doping level is different from critical

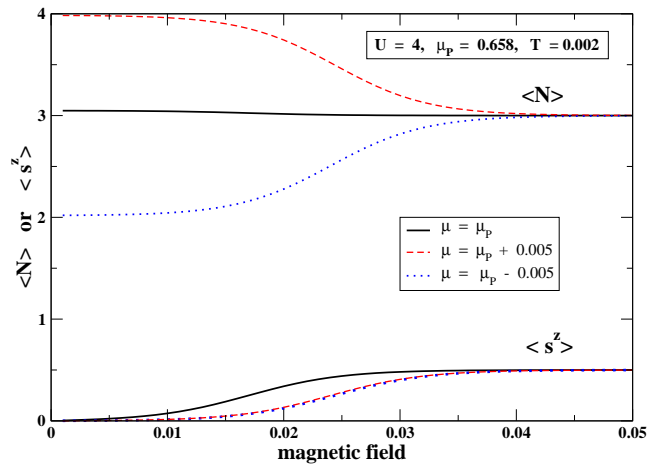


FIG. 4: Variation of electron number  $\langle N \rangle$  and magnetization  $\langle s^z \rangle$  as a function of external magnetic field for several values close to the critical doping  $\mu_P = 0.658$  at  $T = 0.002$  and  $U=4$  for the 4-site cluster. Note how the  $\langle N \rangle = 3$  clusters get stabilized in a nonzero magnetic field at low temperature. These results support the recent observation of a dormant magnetic state near optimal doping in hole-doped La cuprates [19].

cal doping, is due to fluctuations between paired states ( $\langle N \rangle = 2$  and  $\langle N \rangle = 4$ ). This low temperature peak is in agreement with specific heat experiments carried out for the HTSCs [17], and is a manifestation of the near degeneracy of the states in the neighborhood of critical doping  $\mu_P$ .

Our calculations may also be used to reproduce the variation of  $T_c(p)$  vs pressure  $p$  in the HTSCs, assuming that  $U$  decreases with pressure [22]. Fig. 3 shows condensation of electron charge below  $T \leq T_P(U)$  with bound charge  $2e$  and decoupled spin  $\langle s^z \rangle = 1/2$  for the 4-site cluster. Below the lower curve  $T_S(U)$ , the spin degrees are bounded and a finite applied magnetic field is needed to break them [10, 15]. Thus below  $T \leq T_S(U)$ , both the charge and spin are condensed and the spin degrees can follow those of charge. The inset in Fig. 3 shows the variation of the charge gap,  $E(2) + E(4) - 2E(3)$ , as a function of  $U$  where  $E(N)$  refers to the canonical energies for  $N$  electrons at  $T = 0$ . When this gap is negative, pairing is favored as discussed in Ref. [15]. In addition, the increase of  $T_S(U)$  reproduces  $T_c$  (superconducting transition temperature) vs pressure  $p$  in the optimally and nearly optimally doped HTSC materials [18], indicating a significant role of pair binding in enhancing  $T_c(p)$ .

Exact results for  $\langle N \rangle \approx 3$  in Fig. 3 suggest that the enhancement of  $T_c$  in the optimally doped HTSCs may be due to an increase of pairing with decreasing  $U$  under pressure rather than an increase of the pressure-induced hole concentration. Thus it appears that the 4-site cluster near  $\langle N \rangle \approx 3$  indeed captures the essential physics of the electron condensation under pressure.

Another intriguing fact emerging from the exact thermal studies of the 4-site clusters is the existence of a

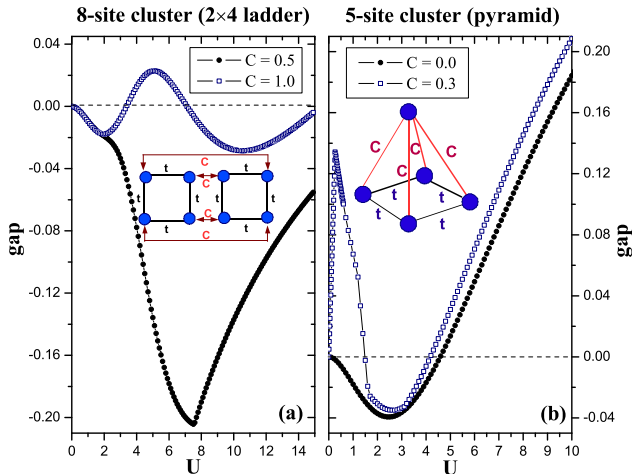


FIG. 5: (a) Charge gaps for the 2x4 cluster at  $T = 0$  for various couplings  $c$  between the squares. (b) Charge gaps for the 5-site cluster illustrate how the coupling  $c$  to a 5th site above the square is responsible for narrowing the window of  $U$  for which pairing exists. In both (a) and (b), the doping level is one electron off half-filling and the couplings  $t$  within the squares are set to 1. Compare these with the inset of Fig. 3.

magnetic state (unpaired states with  $\langle N \rangle = 3$ ) with a large magnetic susceptibility. At rather low temperature  $T \leq T_s^P$ , this state is dormant. However, a small magnetic field or a change in chemical potential can stabilize it over the paired states  $\langle N \rangle \approx 2, 4$  as seen from Fig. 4 and the calculated grand canonical probabilities (not shown). The variation of the magnetic field mimics the doping to some extent here. Small changes in doping (at zero field) can also switch the system from one state to another with a different  $\langle N \rangle$ . These are useful for understanding some recent experimental results reported in Ref [19], where a magnetic (and non-superconducting) state has been observed near 1/8 hole-doping in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ . This system is said to be on the verge of an instability, surprisingly similar to what we observe in these clusters at  $\langle N \rangle \approx 3$  (i.e. near optimal doping away from half-filling).

In order to monitor the size effects on the properties described above for the 4-site cluster, we have carried

out a series of numerical calculations for clusters with different topologies and sizes. Fig. 5 illustrates one such set of calculations of charge gaps done on a 8-site cluster (2x4 ladder), where the hopping term or coupling  $c$  between the two squares was allowed to be different from the coupling within a given square. The pairing fluctuations that are seen for the 4-site cluster exists even for these ladders near half filling ( $\langle N \rangle \approx 7$ ), and most of the trends observed for the 4-site clusters, such as the MH like charge gaps and vanishing of such gaps at critical  $U$  values, remain valid here. The fluctuations that occur here at optimal doping are among the states with  $\langle N \rangle \approx 6, 7$  and 8 electrons. Clearly, the dormant magnetic state corresponds to  $\langle N \rangle \approx 7$ . In addition, a 5-site pyramid with a square base shows a pairing gap when the coupling  $c$  to the fifth site (i.e. the site above the square) is weak (up to about  $0.4t$  where  $t$  is the hopping parameter in the plane) and disappears above this coupling strength.

All of the above, from the 4-site and larger cluster calculations, points to a pair binding instability near optimal doping at relatively low temperature. Thermal and quantum fluctuations in the density of holes between the clusters (for  $U < U_c(0)$ ) make it energetically more favorable to form pairs. In this case, snapshots of the system at relatively low temperatures and at a critical doping level (such as  $\mu_P$  in Fig. 1) would reveal phase separation and equal probabilities of finding in the ensemble of hole-rich or hole-poor clusters only.

In summary, the above results demonstrate the importance of the *many-body interactions* in microscopic clusters. Our exact Hubbard cluster calculations show the existence of charge and spin pairing, electronic phase separation, pseudogaps and condensation and hence demonstrate a rich variety of properties which can be tuned by doping. Furthermore, it is quite surprising to see the number of properties that these exact clusters share with the HTSCs. This may be, at least in part, due to the fact that in all these ‘bad’ metallic high  $T_c$  materials, short-range correlations play a key role.

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